

# Studies on the Flame Photometer for the Determination of $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$ in Portland Cement

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A study has been made on the Perkin-Elmer model 52-A flame photometer to establish its suitability for the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in portland cements and cement raw materials, such as argillaceous limestones and clays. An essential factor in the successful application of the method is the use of suitable standard solutions for each type of material analyzed. Such solutions were developed and excellent results obtained. This paper gives the photometric results due to numerous variables and presents a recommended procedure. On cements, the averages of the differences between the direct-intensity photometric and the gravimetric values obtained were 0.012 percent for  $\text{Na}_2\text{O}$  and 0.024 percent for  $\text{K}_2\text{O}$ . Slightly closer agreement was obtained with the internal-standard method, but uncertainties due to the possible presence of  $\text{Li}_2\text{O}$  give greater reliability to the direct-intensity method. The advantages of flame photometry, both in time and accuracy, are such as to warrant its recommendation for the purpose examined.

## I. Introduction

Flame photometry is an analytical procedure by which a solution to be analyzed is atomized into a flame, and light, characteristic of the element to be determined, is isolated and its intensity measured. In the method of flame photometry, the principles of analytical spectroscopy are applied under conditions that allow rapid determinations to be made with relatively simple apparatus and with personnel having only moderate training.

This method of analysis was advanced several years ago in Europe by Lundegårdh [9],<sup>1</sup> Heyes [7], Schmitt [13], and others. However, it was not until recently that the method of flame photometry was simplified by Barnes and co-workers [2] and a commercial apparatus (Perkin-Elmer Corp., Model 18-A, direct intensity) placed on the market. In a study with this instrument, Parks, Johnson, and Lykken [10] noted a number of sources of error due both to characteristics of the apparatus and to the presence of interfering elements. Berry, Chappell, and Barnes [4] further improved the flame photometer by employing a dual optical system that allowed both the direct-intensity method, and the internal-

standard principle, often used in spectrographic determinations, to be used. By the latter method, the emitted light-intensity ratios of the element sought and of another element introduced in known concentration are measured, rather than the absolute light intensities of the element sought, as is the case with the direct-intensity method. The disturbing effects caused by gas and air-pressure fluctuations, the presence of foreign ions and molecules, and viscosity differences are minimized by the internal-standard procedure. A commercial instrument (Perkin-Elmer Corp., Model 52-A) permitting the use of either method has recently been marketed. Pritchard [12] has compared the two models and voiced the need for further investigation to define a procedure adequate for the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in portland cements.

A study of both methods has been made in this laboratory with the Model 52-A instrument. The purpose of the present paper is to evaluate the results obtained in this study as applied to the determination of soda and potash in portland cement and to present a recommended procedure. The results indicate that the use of the flame photometer for this purpose provides analytical data comparable with those obtained by the best

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

gravimetric methods and has the additional advantage of much greater speed. It is believed that these findings will be generally useful and of benefit, especially to analysts in cement-producing and testing laboratories where the determination of the alkalis constitutes a major problem.

## II. Development of the Method

### 1. Standard Solutions

In applying the flame photometer, it is necessary to provide standard solutions with known alkali concentration and with characteristics such that excitation conditions obtained in the flame are similar to those for the solutions to be analyzed. Such solutions constitute the basis of reference in each determination. It is a matter of common knowledge that the spectral emission of an element may be affected by the presence of other elements in the solution, as also by acidity, viscosity, etc. [4,10]. Thus a spectrographic interference with the measured intensity of the lines of sodium and potassium may be caused by calcium, which has a strong line (5857.46 Å) close to the double sodium line (5895.92-5889.95 Å) and a weaker line (7610.0 Å) close to the potassium lines (7698.98 and 7664.91 Å). The hydrochloric acid that is used to bring the cement into solution may likewise be a source of interference. Other weak lines of calcium, iron, and magnesium appear near the principal lines of the alkalis in an arc spectrum but, at the much lower temperature of the air-propane flame (as recommended for the flame photometer), no interference seems likely to occur.

It would appear that the ideal standard solution, from the point of view of balancing the interference from various elements, would be one composed of the same elements and in about the same concentrations as are found in the cement solutions to be analyzed. Such standard solutions could be approximated by the addition of definite amounts of NaCl and KCl to a solution of a cement of known (by gravimetric analysis) but low alkali content. Solutions were accordingly made<sup>2</sup> from a laboratory-prepared portland cement,<sup>3</sup> which contained (by gravimetric analysis) no potash and only a trace of soda. A tabulation of the gravimetric and photometric values for Na<sub>2</sub>O and K<sub>2</sub>O in a series of portland cements,

using these solutions in conjunction with the internal-standard method, is shown in columns 2 and 5 of table 1.<sup>4</sup> Agreement between the values obtained by the two methods is seen (col. 8) to be excellent, the average of the differences on the basis of the original cements being 0.02 percent for Na<sub>2</sub>O and 0.03 percent for K<sub>2</sub>O.

It was recognized, however, that there are serious objections attached to the use of a cement for making up the standard solutions.

In the first place, cements containing less than 0.1 percent of both Na<sub>2</sub>O and K<sub>2</sub>O are not commonly available, and any error in the values of those oxides, assigned by gravimetric determina-

TABLE 1. Comparison of gravimetric and flame-photometric values for Na<sub>2</sub>O and K<sub>2</sub>O on a series of portland cements, using the internal-standard procedure with standard solutions of different composition

1	2	3	4	5	6	7	8
Cement No.	Gravimetric	Flame photometric with standard aqueous solutions of NaCl and KCl			Difference		
PCA 5-types series 308	Berk-roller	No additions	CaO +HCl	Low-alkali cement +HCl	Column 3-2	Column 4-2	Column 5-2
Percent of Na <sub>2</sub> O							
15394.....	0.42	0.46	0.45	0.42	+0.04	+0.03	0
15396.....	.24	.27	.25	.20	+ .03	+ .01	- .04
15482.....	.29	.32	.32	.27	+ .03	+ .03	- .02
15559.....	.28	.32	.33	.26	+ .04	+ .05	- .02
15399.....	.39	.43	.40	.36	+ .04	+ .01	- .03
15591.....	.21	.19	.17	.15	- .02	- .04	- .06
15614.....	.10	.12	.13	.10	+ .02	+ .03	0
*43.....	1.04	b1.15	b1.10	1.05	+ .11	+ .06	+ .01
Averages...	-----	-----	-----	-----	±0.04	±0.03	±0.02
Percent of K <sub>2</sub> O							
15394.....	0.74	0.59	0.66	0.67	-0.15	-0.08	-0.07
15396.....	1.03	.89	1.02	1.05	- .14	- .01	+ .02
15482.....	0.48	.43	0.43	0.44	- .05	- .05	- .04
15559.....	.49	.44	.46	.48	- .05	- .03	- .01
15399.....	.57	.55	.55	.57	- .02	- .02	0
15591.....	.14	.10	.10	.10	- .04	- .04	- .04
15614.....	.28	.20	.24	.22	- .08	- .04	- .06
*43.....	.08	.08	.09	.08	0	+ .01	0
Averages...	-----	-----	-----	-----	±0.07	±0.035	±0.03

<sup>a</sup> No. 43 PCA Long-Time Series [8].

<sup>b</sup> Beyond range of standard solutions; approximated by dilution.

<sup>4</sup> Gravimetric determinations on cements reported in tables 1, 3, 4, and 5 were made in the laboratory of the Portland Cement Association, Chicago. Some of these data have been published [8].

<sup>2</sup> See below for a detailed description of the methods of preparation of the solutions.

<sup>3</sup> PCAF cement K5-3S2, Lot No. 14646.

tion, would be reflected in all photometric determinations subsequently obtained by their use. Furthermore, if  $\text{Li}_2\text{O}$  is present, it will introduce an error in the gravimetric value for  $\text{Na}_2\text{O}$  as commonly determined, because the value determined for  $\text{Na}_2\text{O}$  includes any  $\text{Li}_2\text{O}$  that is present.

The use, as standard solutions, of water solutions of  $\text{NaCl}$  and  $\text{KCl}$  was found, as anticipated, to give less reliable analytical results than those just reported. A number of such data, making use of the internal-standard procedure, are shown in table 1, where the gravimetric and photometric determinations are set down for a series of cements in columns 2 and 3 respectively, and compared in column 6.

A series of standard solutions was then prepared so as to contain calcium ion and hydrochloric acid in approximately the same concentration as would occur in the solutions of portland cement to be analyzed. These were composed of 6,000 ppm  $\text{CaO}$  (using low-alkali  $\text{CaCO}_3$ <sup>5</sup>) and 50 ml of  $\text{HCl}$  per liter, to which pure  $\text{NaCl}$  and  $\text{KCl}$  were added in such amounts as to give both  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  concentrations in the solutions ranging from 10 to 100 ppm (equivalent to 0.10 to 1.00% of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in 1-g samples of the cements). The above concentration of  $\text{CaO}$  (equivalent to 60% of  $\text{CaO}$  in the cements to be analyzed) is believed to be as satisfactory as any other concentration since, at these high concentrations, a variation of a few percent in the  $\text{CaO}$  content of the cements has no significant effect on the analytical results for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . The analytical values on a series of portland cements obtained with the use of these standard solutions are given in column 4 of table 1, and compared with the gravimetric values in column 7. The agreement with the latter values is seen to be practically as good as that obtained with the use of standard solutions prepared from the low-alkali cement.

From the results discussed above it was concluded that:

The use of a lithia-free low-alkali cement in the preparation of the standard solutions gives photometric values for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  that are in somewhat closer agreement with results obtained by gravimetric analysis than does the use of  $\text{CaO-HCl}$  standard solutions.

<sup>5</sup> The calcium carbonate should meet the specifications for the ACS low-alkali  $\text{CaCO}_3$ , which carries a limit of 0.020% of total alkalies as sulfate. The purchaser should assure himself that the material used meets the specification.

The general unavailability of accurately analyzed lithia-free low-alkali cements makes the use of commercial cements for the preparation of standard solutions of questionable merit.

The excellent agreement between values for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  obtained by gravimetric analysis, and values obtained with the flame photometer making use of  $\text{CaO-HCl}$  standard solutions, warrant the recommendation of such solutions as standards in the flame photometric determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in portland cement.

## 2. Concentration of Internal Standard

The concentration of  $\text{Li}_2\text{O}$  as nitrate as the internal standard used in the above tests was 100 ppm, in accordance with the recommendation of the manufacturer [11]. A series of determinations was made to note if changes in the concentration level of this material, maintained identical of course in the standard and the unknown solutions, had any effect on the photometric results obtained for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .<sup>6</sup> The standard solutions were prepared with the use of the low-alkali cement. The determinations were made by both procedures with lithia added to the standard solutions. The results are shown in table 2, where the concentration of  $\text{Li}_2\text{O}$  as nitrate varied between 50 and 200 ppm. No significant effects on the analytical values for either  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  were observed due to this variation in the concentration of the lithia. As a result of this series of tests, it was concluded that the concentration of 100 ppm  $\text{Li}_2\text{O}$  as nitrate would be satisfactory.

## 3. Viscosity of Solutions

Since the light intensity emitted is a function of the amount of liquid projected into the flame at any moment, and the latter is a function of the viscosity of the solution, it was felt necessary to compare the viscosities of the solutions employed as standards with those of the cements to be analyzed. The time of flow was accordingly measured for 5 ml of such solutions through an Ostwald viscosimeter in a constant-temperature bath at 29° C. The solution of low-alkali cement required 163.2 sec; the  $\text{CaO-HCl}$  solution, containing 100 ppm each of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  as chlorides and  $\text{Li}_2\text{O}$  as nitrate, required 161.7 sec. As

<sup>6</sup> In the "Long-Time Series" [8] of portland cements examined in this study, the lithium content (as  $\text{Li}_2\text{O}$ ) had been shown spectroscopically to be less than 0.05% [6].



TABLE 2. *Effect of varying concentration of Li<sub>2</sub>O (as nitrate), used as internal standard, on Na<sub>2</sub>O and K<sub>2</sub>O determined. Low-alkali cement used in preparation of standard solutions*

Cement No.	Gravi- metric	Internal standard			Direct intensity		
Long-time series [8]	ASTM	Concentration of Li <sub>2</sub> O			Concentration of Li <sub>2</sub> O		
		50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm
		Percent of Na <sub>2</sub> O					
11-----	0.21	0.21	0.21	0.21	0.22	0.23	0.22
23-----	.59	.60	.62	.63	.63	.57	.63
31-----	.23	.24	.23	.24	.26	.22	.26
43A-----	.33	.38	.33	.39	.39	.34	.37
51-----	.08	.08	.07	.07	.07	.07	.08
Percent of K <sub>2</sub> O							
11-----	0.51	0.49	0.57	0.50	0.54	0.52	0.54
23-----	.14	.13	.15	.12	.12	.13	.12
31-----	.22	.22	.26	.21	.23	.25	.23
43A-----	.01	.01	.02	.01	.01	.02	.01
51-----	.22	.27	.27	.25	.25	.26	.24

a basis of reference, distilled water was found to require 155.4 sec. The viscosity difference between the CaO-HCl solution and the cement solution appears to be so small as to be insignificant.

#### 4. Flame Characteristics

It is essential that the gas employed for producing the flame in the photometer be of constant composition and pressure and free of materials that may cause interferences in the spectral emission. It is also desirable that the flame temperature be such that the alkali elements will be readily excited, whereas other elements that require higher temperatures for excitation will not be excited. Complete separation cannot be made of the alkali elements from the alkaline-earth elements present by such control of temperature as is possible with a selection of the gas, but some advantage can be expected from a judicious selection. Excitation of the other metallic elements can be almost entirely avoided [2].

Gas from the city mains was tried with the earlier (model 18) instrument but was found to give rise to a variable flame and erratic analytical results. The pressure also was inadequate for best performance in the burner. Of the gases commonly available in steel cylinders (bottled

gas), acetylene and propane (under various trade names) have been used by various investigators. The flame temperature of acetylene burning in air is much higher than that of propane [14] and results in greater excitation of the nonalkali elements [2]. Propane appears to be nearly ideal for the purpose of exciting the alkali elements with a minimum of interference from other causes, and was employed in these studies.

### III. Analytical Results

#### 1. Precision of Flame-Photometric Method

A group of five cements was subjected to repeated analysis for Na<sub>2</sub>O and K<sub>2</sub>O by use of the

TABLE 3 *Flame-photometric values for Na<sub>2</sub>O and K<sub>2</sub>O in portland cements obtained by two operators over a period of several weeks, and employing varying concentrations of internal standard, to indicate reproducibility of the analytical results under average laboratory conditions*

Internal-standard procedure with low-alkali cement standard

Cement No.	Na <sub>2</sub> O		K <sub>2</sub> O	
	Value determined	Standard deviation	Value determined	Standard deviation
11.....	%		%	
	0.21	0.007	0.50	0.023
	.21		.48	
	.20		.49	
	.21		.50	
	.22		.54	
23.....	.22	.015	.54	.011
	.62		.15	
	.61		.12	
	.59		.13	
	.63		.12	
31.....	.63	.013	.12	.007
	.23		.22	
	.25		.22	
	.23		.22	
	.24		.21	
43A.....	.26	.017	.23	.000
	.26		.23	
	.34		.01	
	.38		.01	
	.38		.01	
51.....	.39	.005	.01	.011
	.37		.01	
	.39		.01	
	.07		.26	
	.08		.27	
Average.....	.08	0.012	.27	0.013
	.07		.27	
	.08		.25	
	.07		.24	
	.07		.25	



flame photometer over a period of several weeks, using the internal-standard procedure with the low-alkali-cement standard solutions. These tests represent the accumulated analytical values on these cements obtained by two operators using various concentrations of  $\text{Li}_2\text{O}$  as an internal standard. The data are set down in table 3 as an indication of the reproducibility of the photometric values even under conditions far from ideal. The standard deviation is seen to vary from 0.005 to 0.017 for  $\text{Na}_2\text{O}$  and from 0.000 to 0.023 for  $\text{K}_2\text{O}$ . The maximum spread for any cement was 0.05 percent for  $\text{Na}_2\text{O}$  and 0.06 percent for  $\text{K}_2\text{O}$ , based on the original sample.

A comparable series for study of the reproducibility of the alkali values by gravimetric methods is not known to be available, but it is believed that the photometric values given will compare favorably with any similar series of gravimetric determinations.

## 2. Reproducibility by Different Operators

The flame-photometric results on a series of cements obtained by three operators using two

different units of the model 52-A instrument are shown in table 4. The agreement between operators (col. 10) is generally satisfactory, the average maximum variation from operator to operator being 0.03 percent for  $\text{Na}_2\text{O}$  and 0.04 percent for  $\text{K}_2\text{O}$ . The average of the differences between the values obtained by the photometric and the ASTM chemical method (col. 9) is only 0.02 percent for  $\text{Na}_2\text{O}$  and 0.01 percent for  $\text{K}_2\text{O}$ .

These results indicate that the personal factor in operating the flame photometer is small and that a high degree of training for an operator is not necessary. Operators *b* and *c* had less than 2 days previous experience with the instrument when the determinations were made.

## 3. Comparison of Photometric and Gravimetric Methods

There are also shown in table 4 gravimetric values on these cements by two different methods, the ASTM standard [1] and the modified Berk-Roller [3]. These two methods are given because the former is usually conceded to be more accurate, whereas the latter is more rapid. It will be noted

TABLE 4. Analytical values for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  obtained by two gravimetric methods and by three operators using the flame photometer direct-intensity method,  $\text{CaO-HCl}$  standard

1	2	3	4	5	6	7	8	9	10	11
Cement No.	Gravimetric			Flame photometer					Comparisons	
Long time series [8]	ASTM	Berk-Roller	Difference 3-2	Operator <sup>a</sup>			Avg. a, b, c	Difference 8-2	Maximum variation between a, b, and c	Maximum variation between 2 and a, b or c
				a	b	c				
Percent of Na <sub>2</sub> O										
11.....	0.21	0.24	+0.03	0.21	0.22	0.18	0.20	-0.01	0.04	0.03
23.....	.59	.66	+ .07	.62	.63	.65	.63	+ .04	.03	.06
31.....	.23	.28	+ .05	.24	.26	.23	.24	+ .01	.03	.03
43A.....	.33	.38	+ .05	.34	.38	.36	.36	+ .03	.04	.05
51.....	.08	.08	0	.08	.08	.05	.07	- .01	.03	.03
Averages.....	-----	-----	+0.04	-----	-----	-----	-----	±0.02	0.03	0.04
Percent of K <sub>2</sub> O										
11.....	0.51	0.59	+0.08	0.56	0.54	0.50	0.53	+0.02	0.06	0.05
23.....	.14	.15	+ .01	.15	.12	.09	.12	- .02	.06	.05
31.....	.22	.26	+ .04	.25	.23	.19	.22	0	.06	.03
43A.....	.01	.04	+ .03	.02	.01	.01	.01	0	.01	.01
51.....	.22	.27	+ .05	.26	.24	.23	.24	+0.02	.03	.04
Averages.....	-----	-----	+0.04	-----	-----	-----	-----	±0.01	0.04	0.04

<sup>a</sup> Operators a and b used the same instrument; operator c, a different instrument.

that the average of the differences obtained by the two gravimetric methods (col. 4) is 0.04 percent for both  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , with maximum individual differences of 0.07 percent for  $\text{Na}_2\text{O}$  and 0.08 percent for  $\text{K}_2\text{O}$ . The more rapid Berk-Roller method gives values for both  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  that are consistently somewhat higher than those obtained by the ASTM method. The photometric results also agree closely with the gravimetric results and in general conform best with those obtained by the ASTM procedure. The average differences between the gravimetric and photometric values (col. 11) are 0.04 percent for both  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . It may here be noted that the gravimetric values, though serving as the basis of reference, cannot be considered as necessarily accurate. The outstanding advantage of the photometric procedure over either gravimetric method is found to lie in the greatly shortened time required for the determination.

#### 4. Comparison of Direct-Intensity and Internal Standard Procedures

Values for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  obtained on 10 cements by both the internal-standard and direct-intensity procedures are given in table 5. The standard solutions for the former were prepared from the low-alkali cement and for the latter from the  $\text{CaO-HCl}$  solution. For comparison, gravimetric determinations by the ASTM standard method [1] are also included. Averages of the differences between the values thus obtained are given at the bottom of the table.

The average of the differences between the flame-photometric determinations using the internal standard and the ASTM gravimetric values (col. 5) is only 0.009 percent for  $\text{Na}_2\text{O}$  and 0.016 percent for  $\text{K}_2\text{O}$ . Using the direct-intensity procedure, the average of the differences (col. 6) is slightly greater, being 0.012 percent for  $\text{Na}_2\text{O}$  and 0.024 percent for  $\text{K}_2\text{O}$ . The average of the differences between the internal-standard and direct-intensity results (col. 7) is 0.005 percent for  $\text{Na}_2\text{O}$  and 0.012 percent for  $\text{K}_2\text{O}$ . Values obtained for  $\text{Na}_2\text{O}$  with the flame photometer by both procedures are in somewhat better agreement with gravimetric values than those for  $\text{K}_2\text{O}$ . In either case, the flame-photometric results compare favorably with the gravimetric values.

From these data, as also those shown in table 2, the results obtained by the internal-standard pro-

TABLE 5. Comparison of analytical results obtained by the internal-standard procedure, using low-alkali cement standard solutions, and by the direct-intensity procedure, using  $\text{CaO-HCl}$  Standard solutions

1	2	3	4	5	6	7
Cement No.	Gravimetric	Flame photometer		Comparisons		
Long-time series [8]	ASTM	Internal standard	Direct intensity	3-2	4-2	4-3
Percent of $\text{Na}_2\text{O}$						
11	0.21	0.21	0.21	0	0	0
13	.04	.05	.05	+0.01	+0.01	0
18	.12	.13	.13	+0.01	+0.01	0
23	.59	.62	.62	+0.03	+0.03	0
25	.21	.21	.22	0	+0.01	+0.01
31	.23	.23	.24	0	+0.01	+0.01
34	.28	.28	.29	0	+0.01	+0.01
42	.16	.13	.13	-0.03	-0.03	0
43A	.33	.33	.34	0	+0.01	+0.01
51	.08	.07	.08	-0.01	0	+0.01
Averages ---	---	---	---	$\pm 0.009$	$\pm 0.012$	$\pm 0.005$
Percent of $\text{K}_2\text{O}$						
11	0.51	0.50	0.56	-0.01	+0.05	+0.06
13	.19	.19	.19	0	0	0
18	.13	.15	.14	+0.02	+0.01	-0.01
23	.14	.15	.15	+0.01	+0.01	0
25	.54	.56	.58	+0.02	+0.04	+0.02
31	.22	.22	.25	0	+0.03	+0.03
34	.28	.30	.30	+0.02	+0.02	0
42	.26	.30	.30	+0.04	+0.04	0
43A	.01	.01	.01	0	0	0
51	.22	.26	.26	+0.04	+0.04	0
Averages ---	---	---	---	$\pm 0.016$	$\pm 0.024$	$\pm 0.012$

cedure are seen to be in slightly better agreement with the ASTM values than those obtained by the direct-intensity method. This difference is small and usually insignificant.

There is, however, an important reason for considering the direct-intensity method to be the more reliable for portland cements and cement raw materials. The internal-standard procedure involves the introduction to the standard and the unknown solutions of a fixed amount of some element by means of which intensity ratios of the alkali elements to the standard are measured. The characteristics of this element are severely restricted; it must be readily excited in the photometer flame, it must not emit spectral lines that would interfere with those of sodium and potassium, and it must not be a constituent of the cements used as stand-

ards or to be analyzed. The only element thus far found partially to meet these requirements is lithium [4], but unfortunately lithium is present in some raw materials that may be used in cement manufacture. Since, in the internal-standard procedure, the measured ratio between the intensity of the lithium (added in a fixed concentration) and of the sodium and potassium (being determined) is the basis for the establishment of the concentration of the latter elements, it is obvious that the concentration of the lithium must be identical in the standard and the unknown solutions. And since the cements being tested may contain lithia in small but unknown concentration, the measurement of the above ratio will not, when lithia is present in the cements being tested, correctly indicate the  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  concentrations. Because of this uncertainty, the internal-standard method is not recommended for the flame-photometric determination of the alkalies in portland cement or cement raw materials, and only the direct-intensity method will be included in the procedure outlined below.

#### IV. Application to Raw Materials

The principal differences between the flame-photometric analysis of a portland cement and of a raw material, such as a clay, are concerned with the increased difficulty of getting the latter into solution and of making a proper selection of materials to be used in preparing the standard solutions.

A flint clay, a plastic clay, and an argillaceous limestone were selected for photometric analysis. These were NBS standard samples for which complete gravimetric analyses were available. It should be pointed out, however, that cement raw materials vary considerably from location to location, and probably no individual material can be considered as representative of a type. Some modifications of the procedure followed here may be necessary for other materials.

An attempt was made to dissolve these materials by the Glaze method [5] using nitric, perchloric, and hydrofluoric acids. By this method, the minerals of the argillaceous limestone were completely dissolved, and the graphite and organic matter were burned off during ignition of the solid perchlorates. This procedure failed, however, to decompose the clays. The latter were ac-

cordingly subjected to sintering with  $\text{NH}_4\text{Cl}$  and  $\text{CaCO}_3$  (J. Lawrence Smith procedure [1]), extracted several times with boiling distilled water and filtered. By this means the alkalies in these clays were brought into solution.

The standard solutions required for a particular type of raw material will depend on the chemicals employed to dissolve the material and the concentration range of the alkalies. Sometimes the resulting solution contains only water and the alkalies; in other cases interfering substances, such as  $\text{CaO}$ , may also be present. In case only sodium and potassium are in solution, standard solutions of the alkalies in water may be prepared of several concentrations up to the maximum amounts of the alkalies expected in the raw material. An alternative procedure in samples of high-alkali content (more than 1%), is to dilute the sample to the concentration range of the usual standard solutions (0 to 100 ppm).

When interfering substances occur in appreciable amounts in solution with the alkalies, it may be necessary to compensate for them in the standard solutions. This will depend on the accuracy required. As mentioned earlier,  $\text{CaO}$  and  $\text{HCl}$  have been found to constitute the chief interferences in these studies. In many cases it may be easier to treat the sample with  $\text{HCl}$  before filtering, and then add the amount of  $\text{CaO}$  occurring in the raw material, plus  $\text{HCl}$ , to the standard solution.

The data from a flame-photometric analysis of these materials for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  by the direct-intensity method using  $\text{CaO-HCl}$  standard solutions are given in table 6. Values obtained for the argillaceous limestone, which was the easiest to put in solution, checked closely, within 0.01 percent for both  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , with the average gravimetric determinations. Soda determina-

TABLE 6. *Gravimetric and flame-photometric determinations of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in cement raw materials*

Gravimetric values as reported in certificates of National Bureau of Standards. Flame-photometric direct-intensity method;  $\text{CaO-HCl}$  standards

	Flint Clay NBS Std. 97		Plastic Clay NBS Std. 98		Argillaceous Limestone NBS Std. 1A	
	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$
Average value on certificate (a) .....	0.12	0.54	0.28	3.17	0.39	0.71
Flame-photometric value (b) .....	.10	.47	.25	3.04	.40	.70
(b)-(a) .....	-.02	-.07	-.03	-0.13	+.01	-.01



tions for both clays also checked closely with the gravimetric results, but the potash values showed, on the basis of the original sample, greater variation from the gravimetric results. This is seen to be related to the larger concentration of potassium present, and the percentage variations are not excessive. These results demonstrate the successful application of the flame-photometric method to the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in cement raw materials.

## V. Recommended Procedure for the Determination of $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$ in Portland Cement

In employing flame photometry for the determination of the alkalis in cement, the instrument must first be calibrated with solutions of known concentration. It is convenient to prepare stock solutions of relatively high concentration in amounts sufficient to last for 3 or 4 weeks, and from these to prepare the standard solutions as required. These solutions should be stored in acid-resistant glass containers, such as Pyrex.

### 1. Stock Solutions

A lime-acid stock solution is prepared to contain 63,000 ppm (6.3 %) of  $\text{CaO}$  and 500 ml of  $\text{HCl}$  per liter:

Add 300 ml of water to 112.5 g of  $\text{CaCO}_3$  (see footnote 5) in a 1,500 ml beaker. While stirring, slowly add 500 ml of  $\text{HCl}$ . Cool to room temperature, transfer to a 1-liter volumetric flask, dilute to 1 liter and mix thoroughly.

A second stock solution is required containing 1,000 ppm (0.1 %) of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , both soda and potash being included in the same solution:

Dissolve 1.8858 g of  $\text{NaCl}$  and 1.5830 g of  $\text{KCl}$  (previously dried at  $105^\circ$  to  $110^\circ \text{C}$  for several hours) in water, dilute to 1 liter in a volumetric flask and mix thoroughly.

### 2. Standard Solutions

Standard solutions are required, for the calibration of the apparatus, which contain known amounts of the alkali oxides together with a concentration of  $\text{CaO}$  and acid approximating that which will be present in the unknown cement solutions. These are prepared by the proper dilution of portions of the stock solutions. Since 1 g of the

cement to be analyzed is dissolved and made up to 100 ml of solution, a  $\text{K}_2\text{O}$  concentration in the cement of 1 percent would be equivalent in the solution to 100 ppm. And since very few cements contain more than 1 percent of either  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ , the usual upper concentration of the alkali oxides in the standard solutions can be fixed at 100 ppm. In the few instances where higher concentrations are encountered, the upper concentration in the standard solutions can be raised as far as necessary, or the solution being analyzed can be further diluted.

In general, the range of 0 to 100 ppm of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in the standard solutions will cover adequately the range of alkali concentrations (0 to 1%) in cements. Although higher sensitivity could be obtained by narrowing the alkali limits in the standard solutions (as between 25 and 75 ppm where the cements contain not less than 0.25 nor more than 0.75% of either alkali oxide), such dilution is not recommended. The likelihood of contamination and consequent erratic results would thereby be greatly increased.

The standard solutions recommended are as follows:

Alkali (as oxide)	Lime-acid solution	$\text{NaCl-KCl}$ solution	Volume of final solution
ppm	ml	ml	ml
100	200	200	2,000
75	100	75	1,000
50	100	50	1,000
25	100	25	1,000
10	100	10	1,000
0	100	0	1,000
100	0	100	1,000

The lime-free solution is for use only in establishing the correct position of the wavelength selector for maximum response to  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . Each alkali solution is measured out, as indicated above, in calibrated pipettes or burettes, but the lime-acid solution may be measured in a graduated cylinder.

### 3. Calibration of the Instrument

With the electric current turned on, the air pressure is adjusted to about 10 psi, the gas pressure to about 5 psi, and the burner lighted. The chimney should be adjusted with its bottom edge

about  $\frac{1}{8}$  to  $\frac{1}{4}$  in. below the top of the burner. The gas and air pressures are further adjusted to give a flame 5 to 6 in. high and having uniform, quiet, greenish-blue cones over the grid of the burner. Under humid conditions, moisture condensation may be prevented by leaving the electrical circuit on continuously. The burner should be on for a half hour before commencing a run.

The internal-standard dial should be set and caused to remain at zero.

The correct position of the wavelength dial is established by pouring lime-free standard solution into the atomizer and moving the selector back and forth on each side of the indicated wavelength for the element until the point of maximum deflection of the meter is obtained. During this operation, the meter is caused to reach the range 90 to 100 by means of the coarse and fine gain controls.

The atomizer should be rinsed with each solution prior to taking readings on that solution.

The 100 ppm alkali lime-containing solution is then poured into the atomizer, and the coarse and fine gain controls adjusted until the meter reads 100. With the alkali-free solution in the atomizer, the zero-adjustment knob is turned until the meter reads zero. These steps should be repeated until the meter needle returns to 100 and 0, respectively, on going from one solution to the other.

The 75-ppm solution is then poured into the atomizer and the meter reading noted. Again the 0 and 100 ppm solutions are tested and the process repeated until consistent results are obtained. The meter reading for the 75-ppm solution is then recorded and the operation repeated with the other standard solutions.

The final recordings for the meter readings of all standard solutions are then plotted on cross-section paper, noting that 10-ppm standard solution represents 0.1 percent of  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  in the cement solutions, 100 ppm represents 1.0 percent, etc.

#### 4. Determination of $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$

When the instrument has been checked against the standard solutions and the calibration curves drawn, the balance of the procedure for the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  concentrations in the cements consists in placing the cements in

solution and comparing meter readings obtained upon such solutions with the calibration curves.

1 g of cement is placed in a 150- to 250-ml beaker and dispersed with 10 to 25 ml of water. 5 ml of  $\text{HCl}$  is added all at once and diluted immediately with 50 ml of water. Any lumps are broken up with a flat-end stirring rod. After digesting for 15 min on a steam bath or hot plate, the solution is filtered into a calibrated 100-ml volumetric flask. The beaker and paper are washed thoroughly with water, the solution cooled and diluted to 100 ml, and this solution mixed thoroughly.

The apparatus is warmed up and adjusted, and the wavelength selector properly placed as in the procedure for calibration. The 100-ppm and alkali-free standard solutions are used for the proper setting of the meter by means of the coarse and fine gain controls, and of the zero-adjustment knob, as previously described.

The cement solution is then poured into the atomizer and the reading noted. The standard solution nearest this reading is then used and its reading noted. If the standard deviates more than one scale division from its former value, the original reading is reestablished by use of the fine gain control. These readings of unknown and nearest standard are repeated until consistent. The reading of the cement solution is then recorded and the  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  concentration read from the appropriate calibration curve.

Each oxide should be reported to the nearest 0.01 percent. Where the combined oxides expressed as  $\text{Na}_2\text{O}$  are required, the  $\text{Na}_2\text{O}$  equivalent of the  $\text{K}_2\text{O}$  is obtained by multiplying the percentage of  $\text{K}_2\text{O}$  by 0.658, recording to nearest 0.01 percent, and adding to the  $\text{Na}_2\text{O}$  as determined.

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WASHINGTON, January 15, 1949.